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(54) Title: AMORPHOUS FERROELECTRIC MATERIALS
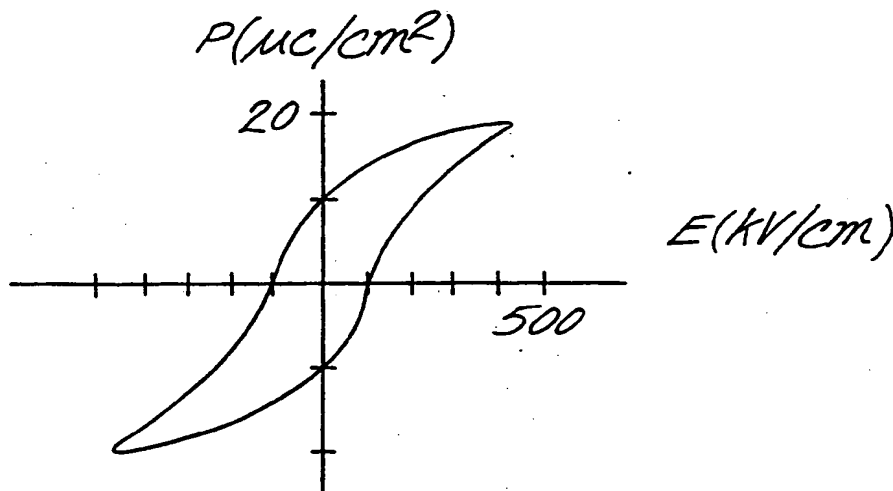
(57) Abstract

Amorphous ferroelectric materials are formed by a sol-gel type process and the ferroelectric properties stabilized by complete hydrolysis and polycondensation, and extraction of residual organic materials, preferably by heating at temperatures below the temperature at which crystallization may occur. Stable solutions of metal alkoxides are prepared by reacting or dissolving a metal alkoxide in alcohol such as absolute ethanol. The solution may be spincast on essentially any substrate, conductor or non-conductor, crystalline or amorphous, transparent or opaque, and even including plastics. Hydrolysis and polycondensation occur in situ to deposit an amorphous ferroelectric film. Residual alcohol is extracted by heating below the temperature at which crystallization occurs. Such films show P-E hysteresis loops and pyroelectric current. Such ferroelectric thin films are useable in electronic, opto-electronic and optical devices.

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AMORPHOUS FERROELECTRIC MATERIALS

Background

This invention relates to ferroelectric materials which are amorphous instead of crystalline. In particular, it concerns a technique for preparing thin films of amorphous ferroelectric material by condensation from a liquid solution containing precursor compounds.

It has been well established that many crystalline mixed oxide compositions such as barium titanate, $BaTiO_3$, $LiNbO_3$, $Pb(Zr,Ti)O_3$, $(Sr,Ba)Nb_2O_6$, and the like, are ferroelectric in nature and both single crystal and polycrystalline forms of these materials have large numbers of practical and potential applications in electronic, opto-electronic, nonlinear optical and piezo-electric devices. Such applications include, for example, optical wave guides, electro-acoustic transducers, high frequency surface acoustic wave devices, pyroelectric infrared detectors, ferroelectric memory cells, ferroelectric photoconductor displays, optical modulators, field effect transistors, metal/insulator/semiconductor transistors and the like.

For many years, it has been believed by the scientific community that ferroelectricity can only exist in a crystalline material with long range order. In 1977, a theoretical discussion suggested that the presence of ferroelectricity in an amorphous glass was

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not excluded on theoretical grounds and a model for a possible amorphous ferroelectric material was proposed. "Microscopic model for a ferroelectric glass" by M.E. Lines, Physical Review B, 15 (January 1, 1977).

Since then, there have been sporadic efforts to produce an amorphous ferroelectric material without apparent success. Techniques for producing amorphous materials have included RF sputtering or in at least one case by extremely rapid quench freezing of molten lithium niobate and lithium tantalate. "Anomalous dielectric behavior and reversible pyroelectricity in roller-quenched $LiNbO_3$ and $LiTaO_3$ glass", by A.M. Glass, M.E. Lines, K. Nassau and J.W. Shiever, Applied Physics Letters, 31 (August 15, 1977). Tantalizing hints of ferroelectricity such as anomalies in the dielectric constant have been noted in amorphous materials. In addition, Glass, et al. noted a pyroelectric response. However, they concluded that "these observations are consistent with ferroelectric behavior, but not conclusive . . . "

To unambiguously show ferroelectricity in a material, it is generally regarded that the most significant indication of ferroelectricity is the well known P-E hysteresis loop. The polarization P as a function of the electric field E shows a characteristic hysteresis loop in an alternating field due to the field required to reverse polarization. Another important criterion is the presence of pyroelectric current, namely current flow from a poled material as temperature is changed.

Ferroelectric materials also have a ferroelectric to paraelectric phase transition temperature T_c sometimes referred to as the Curie temperature. A material may be ferroelectric below the Curie temperature and it loses ferroelectricity abruptly at this temperature. One may also observe ferroelectric domains in the material and a dielectric anomaly is

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likely to be observed. This anomaly may take the form of three or four orders of magnitude increase in dielectric constant near the Curie temperature.

Some of these phenomena may not be observed in a given sample. More than one of these phenomena should be observed to unambiguously determine that there is ferroelectricity. Observation of a P-E hysteresis loop is regarded as proof of ferroelectricity, although it is still desireable to confirm this by observing pyro-electric current and other ferroelectric phenomenon.

Existing metal oxide-based ferroelectrics fall into two general categories, single crystals and polycrystalline ceramics. Single crystals are typically grown from melts at high temperatures by slowly cooling down certain regions of the melt and allowing the growth of a single crystal. A Czochralski technique may be used. Polycrystalline ceramics may be made through solid state reactions of powders or from a melt. Thin films of ferroelectric material may be made in the form of single crystals or in a poly-crystalline form. These thin films have principally been obtained by vapor-phase deposition and sputtering, followed by heating to fully crystallize the deposited film.

It has now been discovered that stable ferroelectricity can be produced in amorphous materials formed by a modified sol-gel technique. The ferroelectric effect has not only been found in mixed metal oxides known to be ferroelectric in their crystalline state, but also in certain single metal oxides never previously known to be ferroelectric. The materials are stabilized, for example, by heating, so that stable ferroelectric properties persist during use of the films.

In recent years, the so called sol-gel technique has been used for preparing crystalline metal oxide-based ferroelectric materials in either thin film

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or powder form. This technique employs organometallic compounds or metal alkoxides to make a homogenous solution. The solution is typically hydrolyzed to produce a gel which may be precipitated, dried and crushed to form a powder, or the solution may be used for coating a thin film on a substrate. The powders or thin films are then heated above a crystallization temperature to produce a polycrystalline ferroelectric material.

Research has been directed to the deposition and crystallization parameters of the technique on the premise that to obtain ferroelectricity full crystallization is necessary. The morphology of the polycrystalline film has been a major concern since it in large part dictates the characteristics of the film. Since there are shortcomings due to grain boundaries in polycrystalline thin films, efforts have also been directed toward growing single crystal films by the sol-gel technique.

It is desirable to have a technique for forming a ferroelectric material which can be processed at low temperatures so that there is greater freedom in selection of materials compatible with processing of the ferroelectric material. It is desirable that the technique for producing the ferroelectric material be suitable for forming thin films for use in modern electronic and optical devices.

Brief Summary of the Invention

Thus, in practice of this invention according to a presently preferred embodiment, an amorphous ferroelectric material is made by preparing a liquid solution containing at least one precursor compound for the ferroelectric material. Solvent is removed to leave an amorphous ferroelectric solid. This solid ferroelectric material is then stabilized at temperatures less than sufficient to crystalize the

1   amorphous material for minimizing changes in ferroelectric properties. During solvent removal, hydrolysis and polycondensation may occur.

5   Amorphous ferroelectric materials include compositions which, when crystallized, have the crystal structure of known ferroelectric crystals, such as $BaTiO_3$ $(Sr,Ba)Nb_2O_6$, $LiNbO_3$, $Pb(Zr,Ti)O_3$ and $(Pb,La)(Zr,Ti)O_3$. The ferroelectric materials include nonstoichiometric mixed metal oxides such as

10 $2[Li_xNb_{(1-x)}O_y]$ where x is in the range of from 0 to 0.5 and $y = (5-4x)/2$ and $Pb(Zr_xTi_{(1-x)})O_3$ where x is in the range of from 0 to 1. The first example includes a single metal oxide Nb_2O_5. Other single oxides in amorphous form which show P-E hysteresis include ZrO_2,

15 SnO_2, TiO_2, Y_2O_3, BaO, SiO_2 and B_2O_3, for example. The ferroelectric effect is independent of the substrate on which a thin film is deposited and the substrate may include organic polymers such as electrically conductive polymers. Electronic, optoelectronic and

20 optical devices may employ amorphous ferroelectric films.

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Brief Description of the Drawings

These and other features and advantages of the present invention will be appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIG. 1 illustrates an exemplary P-E hysteresis loop of an amorphous ferroelectric material;

FIG. 2 illustrates pyroelectric current of an amorphous ferroelectric film;

FIG. 3 illustrates an exemplary electronic device employing an amorphous ferroelectric film;

FIG. 4 illustrates an exemplary optoelectronic device employing a ferroelectric film; and

FIG. 5 illustrates an exemplary optical device employing an amorphous ferroelectric thin film.

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Detailed Description

Very generally speaking, a sol-gel process for forming an amorphous ferroelectric material starts with formation of a solution containing one or more organo-metallic compounds forming a precursor for the thin film. For example, for a binary metal oxide ferroelectric, the solution may contain appropriate proportions of two metal alkoxides which may react to form a double metal alkoxide, or which may remain separately in solution. In some cases, water may be added to the solution to cause formation of a gel.

Such a solution or gel may be applied to a substrate to form a thin film or the gel may be dried in bulk. The dried solid may be pulverized to form a ferroelectric powder. Alternatively, the metal alkoxide solution may be applied to a substrate to form a thin film and hydrolyzed in situ to form an amorphous ferroelectric thin film.

The amorphous ferroelectric material is stabilized, typically by heating to a relatively low temperature in a suitable atmosphere for complete hydrolysis and removal of organic materials.

An example of the formation of a ferroelectric thin film involves stoichiometric lithium niobate, $LiNbO_3$, which is known to be a ferroelectric in its crystalline state. Lithium metal is reacted with absolute ethyl alcohol, forming a solution of $LiOC_2H_5$. A typical concentration of the lithium ethoxide is in the range of from 0.2 to 0.6 Mol/l. To this solution, there is added an equal amount of $Nb(OC_2H_5)_5$ in the form of a commercially available 99.99% pure liquid. The niobium ethoxide may be simply poured into the lithium ethoxide solution since precipitation is not a problem. The solution is then boiled and refluxed for 24 hours with a water cooled reflux condenser.

Lithium and niobium ethoxides are known to form an intermolecular complex sometimes referred to as a

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double alkoxide upon extensive refluxing. This double alkoxide, which is soluble in ethyl alcohol, in its crystalline form closely resembles the local atomic configuration of crystalline $LiNbO_3$. In the ethyl alcohol solution, the $LiNb(OC_2H_5)_6$ double alkoxide is stable and may be detected by FTIR and NMR. Hydrolysis and polycondensation of the double alkoxide produces a lithium niobate having the composition of the alkoxide precursors.

The entire synthesis, mixing and reflux is conducted in a dry nitrogen glove box. Reflux may also be conducted outside a glove box with a thorough desiccant connected to the outlet of the condenser. It is important for maintaining shelf life to avoid introduction of water. Preferably air is excluded to exclude water vapor. A small amount of water may reduce the shelf life of the solution to a few days or even hours whereas a solution substantially free of water and isolated from the air as an essentially unlimited shelf life.

A solution prepared in this manner may then be used for coating a thin film on a selected substrate by conventional spin casting. In this technique, a substrate is secured to a spinner, typically with a vacuum chuck. The substrate is rotated at a selected speed to spread a liquid in a thin film. The thickness of the film obtained depends on a number of parameters including rotation speed (higher speed produces a thinner film), solute concentra-tion (increased concentration of the organometallic produces an increased thickness), relative humidity (higher humidity produces a thicker film), and temperature (generally speaking, higher temperature produces a somewhat thinner film).

It is desirable when casting and hydrolyzing the thin films of amorphous ferroelectric material to have a low relative humidity. Preferably, the relative

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humidity in the air during casting and initial hydrolysis is in the range of from 10 to 25%. Some humidity is desirable to assure hydrolysis and polycondensation of the ferroelectric material. High relative humidity may induce such rapid hydrolysis that the homogeneity of the film is jeopardized. Very high relative humidity may also produce a thick film that is subject to cracking. A relative humidity as high as 50% may be tolerated for some films. Hydrolysis in such a high relative humidity may be largely complete in a minute or so. The hydrolysis reaction occurs rapidly, but evaporation of the resultant alcohol may be impeded.

Film thicknesses from 500 to 6000 Angstroms may be formed. If desired, a thicker film may be obtained by permitting the film to stand in air for a sufficient period to largely complete hydrolysis at least at the surface. The hydrolyzed solid is essentially insoluble in the solution. Substantially complete hydrolysis can be obtained in no more than a few minutes, then another drop of solution may be added to the substrate on the spincaster. If one tries to produce too thick a film with this technique, there may be cracking.

If desired, one may make a thicker film in several layers with stabilization of the underlying films. With intermediate stabilization of the film by heating, cracking may be minimized.

When the metal alkoxide is contacted by water, such as the water vapor present in air, there is polycondensa-tion of a polymer having metal-oxygen-metal bonds. The alkyl group is released as the corresponding alcohol. Typically the solvent used is the same as the alcohol released.

When water is added to the solution before forming a thin film, a prepolymer may be formed as particles in a gel. The gel may be completely hydrolyzed and solvent extracted to form a more or less solid body.

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Such a body may be crushed to form a ferroelectric powder. The prepolymer may be coated on a substrate by spraying, dipping, spincasting, or the like, with hydrolysis and complete polymerization occurring in situ on the substrate.

When dipping film thickness is controlled by speed of withdrawal of the substrate from the solution, temperature, solute concentration, and relative humidity. Ordinary, normal room temperature and humidity conditions fall within the desired temperature and humidity range for dip coating.

Prepolymerization by adding water to the solution may reduce the shelf life of the solution. It may also lower the crystallization temperature of the amorphous material. Thus, it is preferred to deposit films from solutions free of water, or at best, with water added only a short time before deposition.

After spincasting, the film is stabilized for minimizing future changes in ferroelectric properties. The as-cast film includes organic materials which may comprise some of the alkoxy compound which is not yet hydrolyzed, the released alcohol from the hydrolysis, and the alcohol solvent. Heating of the amorphous ferroelectric material at a temperature less than sufficient to cause crystallization can quickly stabilize the film. The heating accelerates hydrolysis and vaporization of the solvent. Heating in air at 100°C for as little as two hours can reduce the organic content of the film from about six mol percent to one mol percent. Higher temperatures may be used for stabilization without crystallizing the film. Heating may be in air or an inert atmosphere. Water vapor may be present in the atmosphere during heating to assure complete hydrolysis.

In one example, a thin film of lithium niobate amorphous ferroelectric material had a thickness of about 1100 Angstroms. It was stabilized by heating in

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air for one hour at 200°C. The composition profile of
the film was measured by Auger analysis. The nominal
composition of the film after stabilizing was
$Li_{1.01}Nb_{0.99}(OC_2H_5)_{0.006}O_{2.75}$. Thus, the organic content of
the film was about one percent. The reason for the
apparent deficiency of oxygen is not clear.

It is desirable that the amorphous material be
essentially completely hydrolyzed before appreciable
heating. This is significant to help avoid oxidation
of the organic material with the possible consequence
of producing a metal carbonate which is not ferro-
electric. Generally speaking, oxidation is undesirable
since it tends to reduce the remanent polarization of
the ferroelectric material. If desired, oxidation may
be largely eliminated by casting and hydrolyzing a thin
film of amorphous ferroelectric material in a moist
nitrogen environment.

The ferroelectric properties of a film are
apparently unaffected by the substrate on which the
film is deposited. Indicative of that is confirmation
of ferroelectric properties of films deposited on
amorphous silicon carbide, semiconductors such as
silicon (n-type, p-type or intrinsic) and gallium
arsenide, insulators such as fused quartz, Pyrex
borosilicate glass, aluminum oxide, and magnesium
oxide, metals such as gold, platinum, aluminum, and
iron, conductors such as indium tin oxide, polypyrrole,
and polyaniline, and ferroelectric materials such as
lithium tantalate and single crystal lithium niobate.
This shows the versatility of amorphous ferroelectric
materials for a broad variety of applications.

The ferroelectric material is stabilized by
heating in air to a sufficient temperature to complete
the hydrolysis and drive off remaining organic
material. The temperature required depends on the
thickness of the film, relative humidity, the solvent
employed, reaction products from the precursors,

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temperature resistance of the substrate and the crystallization temperature of the amorphous ferro-electric material.

The as deposited film contains alkoxy and hydroxy groups, for example. These continue to undergo reaction and evaporation after deposition. Although the as deposited films show ferroelectric behavior, the characteristics are not stabilized until these groups are removed or otherwise stabilized.

For example, thin film lithium niobate crystallization commences in the range of from 350 to 450°C depending on conditions. Stabilization of the amorphous material is therefore desirably conducted at a temperature of up to about 250°C to assure that there is no crystallization. The time of heating depends on temperature, with higher temperatures requiring shorter heating cycles. Preferably, the heating rate is in the range of from about 1° to 5°C per minute. A relatively low heating rate is desirable to avoid cracking, with slower rates being preferred for thicker films. Time is required for solvent to diffuse from the film and for structural relaxation to occur. It is noted that during stabilization, shrinkage of as much as 50% of film thickness may occur.

Stabilization may also be obtained by assuring that there is ample exposure to water vapor at room temperature, and the film may be further consolidated by enhancing the evaporation of solvent in a vacuum system.

Heating in air to a temperature in excess of the expected service temperature of the product employing the ferroelectric material remains the preferred technique for stabilizing the film. Stabilizing a film at somewhat elevated temperatures is desireable for producing a relatively dense film. A denser film provides a higher remanent polarization P_r. In the tests to date, values of P_r of from 6 to 18 have been

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observed, which is within the range of ferroelectric thin films currently in use.

The low temperatures needed for stabilizing are particularly attractive for formation of a ferro-electric thin film on a plastic substrate. For example, it has been shown that an amorphous ferro-electric thin film can be formed on electrically conductive polymers such as polypyrrole and polyaniline. This provides the ability to form a somewhat flexible ferroelectric device.

Ferroelectricity may be caused by several entirely different mechanisms. A common feature for all known ferroelectric materials is the existence of electric dipoles prior to the application of an external electric field, wherein the dipole direction can be effectively reversed by application of an electric field. Probably the most commonly mentioned example is a barium titanate crystal, $BaTiO_3$, consisting of oxygen octahedra with a Ti^{4+} cation enclosed near the center of the oxygen octahedron. Because of the size of the ions, there is enough room in such an octahedron for the Ti^{4+} ion to "rattle" between corners of the octahedron. At room temperature, this "rattling cage" remains stationary with the cation off-center near one of the corners of the octahedron. This asymmetry creates an electric dipole.

Under the influence of an external electric field, the relative positions of the Ti^{4+} and O^{2-} ions can be changed so that the center of their corresponding charges shift from the equilibrium positions in the octahedron in opposite directions along the electric field. When the electric field direction reverses, the original dipole direction can in turn be reversed by overcoming a potential barrier. In the case of barium titanate, it is commonly recognized that the potential barrier is caused by the combination of spontaneous polarization of the dipoles on a macroscopic scale

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(usually referred to as the formation of domains) and an inherent potential barrier at a microscopic scale. It is the reversibility of the dipoles and the existence of the potential barrier that results in the well-known P-E hysteresis behavior which is characteristic of ferroelectric materials.

In practice of this invention, the importance of the octahedron structure is recognized. When making an amorphous ferroelectric material, one seeks to recreate the nearest neighbor structure of the corresponding crystalline ferroelectric material and at the same time maintain a long range disorder. With this in mind, one may, through polycondensation of an organometallic compound, produce amorphous ferroelectric films of virtually every known metal oxide-based ferroelectric material.

However, it appears that close resemblance of the local structure to corresponding crystalline ferro-electric materials does not appear to be necessary. A necessary and sufficient condition for ferroelectricity is the existence of a reversible electric dipole and potential barrier that resists the reversal or annihilation of the dipole. Thus, there are a number of amorphous metal oxide systems in both mixed oxides and amorphous single metal oxides which are ferro-electric where it is not certain that an octahedral local structure is present.

Amorphous ferroelectricity has been observed in a broad variety of materials. This has been shown by the P-E hysteresis curves. FIG. 1 illustrates an exemplary P-E hysteresis curve at 50 Hz for a lithium niobate sample deposited on a gold coating on a silicon wafer. The film was stabilized at 250°C for one hour. This is neither the best nor worst hysteresis curve observed, but is merely exemplary.

A modified Sawyer-Tower bridge was used for the P-E hysteresis measurements. Most hysteresis curves

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were observed at 50 Hz. Some observations were made at frequencies as high as 12 kHz for verifying that the hysteresis loops seen were not due to space charge or other possible low frequency effects in the dielectric material.

In a typical hysteresis test set up, the substrate is electrically conductive. A metal "spot" of known area is sputtered on the surface of the thin film. Electrical contact is made to the metal spot and the conductive substrate for connection in the bridge.

In order to exclude any possible interface effects between a gel film and the substrate, a ground powder of bulk gel was used to independently confirm the hysteresis loops. For example, a lithium-niobium ethoxide solution was hydrolyzed and dried. The resultant solid amorphous lithium niobate was pulverized to form a powder and was stabilized at 100°C for two hours in air. The gel powder was dispersed in acetone and dropped on the polished surface of a copper plate. A second copper plate was then pressed onto the other side of the powder layer to form a sandwich with the copper plates forming the electrical contacts for the bridge. The same type of hysteresis loops were obtained for the powder as for a thin film of similar material.

Another independent verification of amorphous ferroelectricity estimated the characteristic Maxwell relaxation time of a thin film deposited on fused quartz and stabilized at 100°C. A relaxation time in the order of 10^4 seconds was estimated, corresponding to 10^{-4}Hz, too slow to contribute to the hysteresis loop measurements which were at 50 Hz and higher. The electrical conductivity was measured at about $10^{-6}/\Omega$-cm.

Another verification of ferroelectricity is illustrated in FIG. 2. A sample of amorphous ferroelectric lithium niobate was poled by cooling from 75°C in a d.c. electric field. After space charges

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were eliminated, pyroelectric coefficient was measured during reheating several hours after poling. FIG. 2 illustrates dP/dT as a function of temperature where P is the peak saturation polarization and the units of the pyroelectric coefficient are nanocoulombs per cm^2K.

That the ferroelectric material was amorphous was confirmed by X-ray diffraction and electron diffraction. An electron diffraction pattern shows only diffuse rings. The observable limit of crystallite size in the X-ray diffraction is approximately 100 angstroms, while that of electron diffraction was 20 Angstroms. No crystallites were observed. Both of these tests indicate the basically amorphous nature of the film. If there were any small crystallites, they were necessarily smaller than 20 angstroms.

Another significant amorphous ferroelectric material comprises barium titanate. The solution for depositing a film of barium titanate is made by first dissolving titanium isopropoxide in isopropyl alcohol. Next, one gradually adds barium n-butoxide gradually while stirring vigorously so that no precipitation occurs. The proportions of barium and titanium in the solution are equal so that a stoichiometric double alkoxide is formed and the solution and barium titanate is condensed. The total concentration is in the range of from 0.2 to 0.6 Mol/1. The solution is refluxed for several hours. It is important to form this solution in the absence of moisture since the composition hydrolyzes quite readily. A double alkoxide forms rapidly with only an hour of reflux. A thin film deposited from the solution forms a ferroelectric amorphous film of barium titanate.

A particularly useful amorphous ferroelectric material is known as PZT, which has the formula $Pb(Zr_xTi_{(1-x)})O_3$, where x is in the range of from 0 to 1. A specific example shown to be ferroelectric comprises

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1    $Pb(Zr_{0.52}Ti_{0.48})O_3$. Precursors for PZT include titanium
     isopropoxide and zirconium n-propoxide. The zirconium
     and titanium alkoxide compounds are mixed in
     isopropanol. Separately, one dissolves lead acetate in
5   isopropanol. The lead isopropanol solution is very
     gradually added to the zirconium-titanium solution with
     vigorous stirring. The solution is refluxed for one to
     eight hours. The solution does not form a double
     alkoxide like the lithium-niobium system, but is a true
10   solution of the three precursor compounds. Refluxing
     is to assure homogeneity rather than to promote
     reaction.

          Another useful amorphous ferroelectric material,
     sometimes referred to in its crystalline form as SBN is
15   strontium barium niobate having the formula
     $(Sr_xBa_{(1-x)})Nb_2O_6$ where x is in the range of from 0.25 to
     0.75. An exemplary composition shown to be ferro-
     electric comprises $(Sr_{0.6}Ba_{0.4})Nb_2O_6$. The solution for
     depositing SBN is made by reacting strontium metal with
20   absolute ethanol to form a first solution of strontium
     ethoxide. A separate solution of barium ethoxide is
     formed by reacting barium metal with absolute ethanol.
     Appropriate proportions of the solutions are then mixed
     together. An appropriate amount of liquid niobium
25   ethoxide is slowly dropped into the mixed solution with
     vigorous stirring. The resultant solution is refluxed
     for about five hours. Typical concentration of the
     solutes in the solvent is in the range of from 0.2 to
     0.6 Mol/l. The SBN precursor composition is extremely
30   sensitive to moisture and the reactions are conducted
     and the product stored in a dry nitrogen environment.
     A thin film of amorphous SBN may then be formed by
     spincasting or by spraying or dipping.

          Other amorphous oxide-based ferroelectric
35   materials may be made by a similar technique of forming
     or dissolving metal alkoxides or other organometallic
     compounds in an organic solvent, and hydrolyzing the

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solute in the resulting solution either in bulk, or during or after deposition as a thin film.

Another useful amorphous ferroelectric material comprises PLZT, a mixed metal oxide of lead, lanthanum, zirconium and titanium. Other ferroelectric materials include $Pb_{0.92}Bi_{0.07}La_{0.01}(Fe_{0.405}Nb_{0.325}Zr_{0.27})O_3$, $LiTaO_3$, $Bi_4Ti_3O_{12}$, potassium niobate, lead zirconate-lead titanate nonstoichiometric solid solutions, lead titanate, lead niobate, lead tantalate, lead bismuth niobate, lithium tantalate, sodium vanadate, silver vanadate, barium lithium oxyfluoaluminate, $Ba(Al_{1.4}Li_{0.6})(O_{2.8}F_{1.2})$, and lead iron niobate, $Pb_2(Fe,Nb)O_6$. Other ferroelectric materials may be produced which have Curie temperatures substantially below room temperature such as potassium tantalate, sodium niobate, cadmium titanate, strontium (pyro)tantalate, tungsten trioxide and the like.

It should be noted from the disclosures above that an amorphous ferroelectric material of mixed metal oxides may be produced with a nonstoichiometric composition. Thus, amorphous ferroelectric materials include $2[Li_xNb_{(1-x)}O_y]$ where x is in the range of from 0 to 0.5 and y is $(5-4x)/2$, $Pb(Zr_xTi_{(1-x)})O_3$ where x is in the range of from at least 0 to 1 and $(Sr_xBa_{(1-x)})Nb_2O_6$ where x is in the range of from 0.25 to 0.75.

The following table shows the compositions and properties of stoichiometric lithium niobate, nonstoichiometric LN compositions and niobium oxide which surprisingly in the amorphous form is ferro-electric.

TABLE 1

Composition	$LiNbO_3$	$Li_{0.33}Nb_{1.67}O_{4.34}$	$Li_{.25}Nb_{1.75}O_{4.5}$ Nb_2O_5
Film Thickness (Å)	2100 2870	2300	2560
P_r ($\mu C/cm^2$)	10 18	14	9
E_c (kV/cm)	110 24	86	65
Refractive Index	1.43 1.15	1.13	1.13
Pyroelectric Coefficient @ 28°C (nC/cm^2 K)	24 8	---	---
Dielectric Constant	5 ---	---	---

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All of the samples listed in the table were deposited as a thin film on a gold substrate (a film of gold on a silicon substrate) for P-E hysteresis measurements. The samples were stabilized at 100°C for two hours in air. The magnitude of the remanent polarization P_r is in the order of 20% of the polarization of single crystal $LiNbO_3$.

The pyroelectric current was measured for the two samples indicated with films deposited on n-type silicon (111) single crystal wafers. The amorphous films were spin-coated on the polished surface of the silicon wafer and stabilized at 100°C for five hours in air. Gold was sputtered onto the surface of the film to form the top electrode with the silicon used as the other electrode.

The sample was then preheated to 75°C and a DC voltage of five volts was applied across the electrode and maintained as the sample was slowly cooled down to room temperature. The five volt bias was removed at room temperature and the electrodes electrically connected through a picoammeter for measuring current while the sample was reheated at a constant heating rate up to 75°C. This allowed measurement of the depolarization current as a function of temperature. After again cooling to room temperature, a third cycle of heating to 75°C was conducted and the pyroelectric current was monitored.

The junction current which is a function of temperature was measured first. After poling the film by cooling with an applied DC voltage, the current was measured during the second heating. This current is a sum of the junction current, a depolarization current and the pyroelectric current. The pyroelectric current is measured on the third heating and from that the pyroelectric coefficient as a function of temperature can be calculated.

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A particularly surprising discovery is that an amorphous film of niobium oxide, Nb_2O_5, deposited from solution is ferroelectric. Further investigation has established that amorphous zirconium oxide, tin oxide, titanium oxide, yttrium oxide, barium oxide, silicon oxide and boron oxide are also ferroelectric and may be stabilized as amorphous ferroelectric materials (e.g. by heating at 260°C for one hour in air). Such materials are not known to be ferroelectric in their crystalline form. This is probably due to the symmetry in their crystalline form which prevents a dipole moment. On the other hand, the amorphous material has distortion that breaks down the symmetry and may be ferroelectric.

It is believed that other single metal oxides in amorphous form as described herein are also ferroelectric including, for example, oxides of vanadium, hafnium, tungsten, lanthanum and the lanthanide metals.

As an example of an amorphous ferroelectric single metal oxide, one can refer again to niobium oxide, Nb_2O_5. A solution for producing amorphous niobium oxide has niobium ethoxide dissolved in absolute ethanol. A thin film of niobium oxide was deposited on n-type silicon (111) and the properties measured. A film having a thickness of 1600 angstroms was spincast and retained at room temperature in air for five hours for hydrolysis and polycondensation. The remanent polarization P_r was 9.7 $\mu C/cm^2$ and coercive field E_c was measured at 3.7 kV/mm. The pyroelectric coefficient was 8.1 nC/cm^2K. X-ray diffraction showed that the film was amorphous.

Another film of the same material was heated for five hours at 350°C in air. The film thickness was 1250 angstroms, P_r was 12.2 and E_c was 5.4. X-ray diffraction showed that this film was also amorphous.

A similar film was heated for five hours at 450°C in air. The film thickness was 1250 angstroms. P_r was

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7.95 and E_c was 6.0. The pyroelectric coefficient was 88. X-ray diffraction showed peaks coincident with those of gamma-phase Nb_2O_5.

Thus, it was shown that gamma niobium oxide has P-E hysteresis behavior indicating its ferro-electricity. P-E hysteresis was also measured using the copper/oxide powder/copper sandwich mentioned above for alpha-phase niobium oxide, gamma-phase niobium oxide, and rutile, TiO_2.

Thus, ferroelectric behavior has been observed for certain crystalline single metal oxides not previously identified as ferroelectric.

Amorphous ferroelectric thin films are useful in a broad variety of electronic, opto-electronic and optical devices where polycrystalline ferroelectric materials may also find utility. Thus, for example, FIG. 3 illustrates an exemplary field effect transistor employing an amorphous ferroelectric thin film. Such a transistor is formed on an n-type silicon substrate 10. P-type dopants are diffused into the substrate to form a source 11 and drain 12. A thin film of amorphous ferroelectric material 13 such as lithium niobate is deposited on the silicon surface between the source and drain. Metal films are deposited to form a source electrode 14 and drain electrode 15 connected to the source and drain, respectively. A metal film gate electrode 16 is deposited on a portion of the gate 13 for control of the transistor. Such an metal\ferroelectric\semiconductor transistor may be a discrete component or a component in an integrated circuit.

FIG. 4 illustrates schematically an opto-electronic, ferroelectric-photoconductor memory device. Such a memory device has a substrate electrode 17 on which is deposited a ferroelectric thin film 18 such as lithium niobate. The amorphous ferroelectric film is surmounted by a conventional deposited photoconductor

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film 19 and transparent electrode 20. The two
electrodes are connected to a drive voltage source 21.
A data signal may be read out across a capacitor 22
connected across the electrodes of the memory device.
Data are written into or read out of the ferroelectric
layer from the memory chip when both voltage pulses are
applied and light is pulsed onto the photoconductor
film through the transparent electrode. Such an opto-
electric device may be incorporated in an integrated
circuit with a variety of other opto-electronic and
electronic components.

In any of the electronic or opto-electronic
devices, it may be highly advantageous to pole the
ferroelectric material by applying an electric field
and cooling the material from a temperature above the
expected surface temperature of the device as described
above.

FIG. 5 illustrates a fragment of an exemplary
optical device employing an amorphous ferroelectric
material. In a simple example, such an optical device
comprises a ferroelectric crystal 23 such as barium
titanate. An amorphous ferroelectric thin film 24 of
barium titanate is deposited on a surface of the ferro-
electric crystal. Since the film is amorphous, it has
a slightly different index of refraction from the
crystal even when chemically similar so that it can
serve as a ferroelectric window. It may be
particularly advantageous in such an optical device to
employ a nonstoichiometric amorphous thin film for
obtaining a desired index of refraction.

Various of the amorphous ferroelectric materials
may be doped with small amounts of other elements for
tailoring the ferroelectric, dielectric and optical
properties for a selected application. It should also
be recognized that the ferroelectric properties such as
P-E hysteresis and dielectric properties of the thin
film may be selected by varying the nonstoichiometric

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composition or by depositing multiple layers of amorphous ferroelectric materials of different composition.

Although a considerable variety of amorphous mixed metal oxides and single metal oxides have been shown to be ferroelectric, it will be understood that additional similar oxides of stoichiometric and nonstoichiometric compositions may have equivalent ferroelectricity. Examples have been given of techniques for forming amorphous ferroelectric materials by a modified sol-gel process. Many additional modifications of the process for producing amorphous ferroelectric materials will be apparent to those familiar with such processes. It is therefore to be understood that within the scope of the appended claims, this invention may be practiced otherwise than as specifically described herein.

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WHAT IS CLAIMED IS:

1. An amorphous ferroelectric material prepared by the steps of:

preparing a liquid solution containing at least one precursor compound for the material;

removing the solvent from the solution for forming a solid amorphous ferroelectric material; and

stabilizing the ferroelectric material for minimizing changes in ferroelectric properties, the stabilizing being conducted at a temperature less than sufficient to crystallize the amorphous material.

2. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material is selected from the group consisting of barium titanate, lithium niobate, strontium barium niobate, lead zirconium titanate, lead lanthanum zirconium titanate, yttrium oxide, zirconium oxide, tin oxide, titanium oxide, barium oxide and silicon oxide.

3. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material is a stoichiometric single metal oxide selected from the group consisting of the oxides of zirconium, tin, titanium, yttrium, barium, silicon, vanadium, hafnium, tungsten, lanthanum and the lanthanide metals.

4. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material is a nonstoichiometric multiple metal oxide, and more specifically, a mixed metal oxide selected from the group consisting of $2[Li_xNb_{(1-x)}O_y]$ where x is in the range of from 0 to 0.5 and $y = (5-4x)/2$, $Pb(Zr_xTi_{(1-x)})O_3$ where x is in the range of from 0 to 1, and $(Sr_xBa_{(1-x)})Nb_2O_6$ where x is in the range of from 0.25 to 0.75.

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5. An amorphous ferroelectric material as recited in any of the preceding claims wherein the amorphous ferroelectric material is in the form of a film on a substrate.

6. An amorphous ferroelectric material as recited in any of the preceding claims wherein the substrate is flexible.

7. An amorphous ferroelectric material as recited in any of the preceding claims wherein the substrate comprises an electrically conductive organic polymer.

8. A method for forming an amorphous ferroelectric material as recited in any of the preceding claims comprising the steps of:
    preparing an anhydrous solution containing at least one precursor compound for the material;
    removing solvent from the anhydrous solution for forming an amorphous solid material; and
    heating the condensed amorphous material at a sufficient temperature for stabilizing its polarization properties and an insufficient temperature for crystallizing the amorphous material.

9. A method as recited in claim 8 comprising the step of depositing the solution as a film on a substrate before completely solidifying the amorphous material.

10. A method as recited in claim 8 wherein the precursor compound comprises a metal alkoxide and comprising the step of exposing the metal alkoxide to water vapor for hydrolysis and polycondensation.

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11. A solid state electronic device comprising:

a substrate;

a circuit component on the substrate, a portion of the circuit component comprising a film of amorphous ferroelectric material as recited in any of the preceding claims; and

means for applying an electric field across at least a portion of the film of amorphous ferroelectric material.

12. A thin film of amorphous ferroelectric material selected from the group consisting of barium titanate, lithium niobate, strontium barium niobate, lead zirconium titanate, lead lanthanum zirconium titanate, yttrium oxide, zirconium oxide, tin oxide, titanium oxide, barium oxide and silicon oxide.

13. An optical device including a transparent film of amorphous ferroelectric material.

14. An optical device comprising:

a crystalline ferroelectric substrate; and

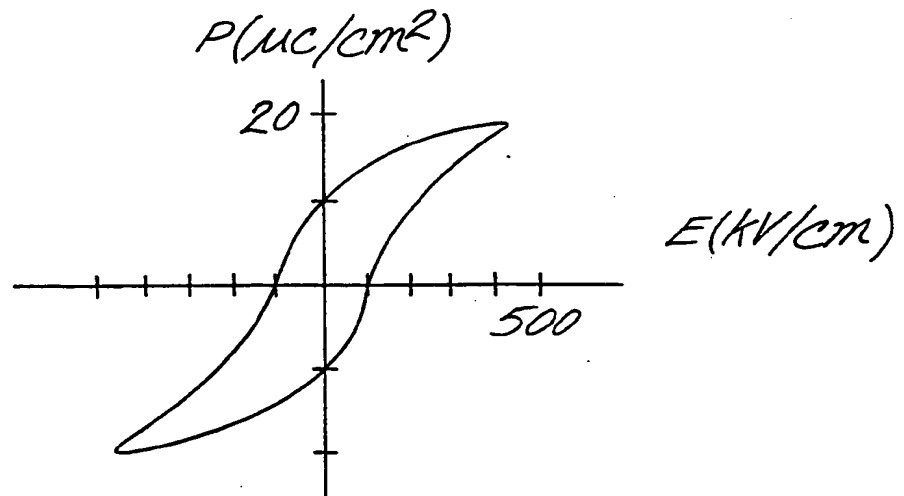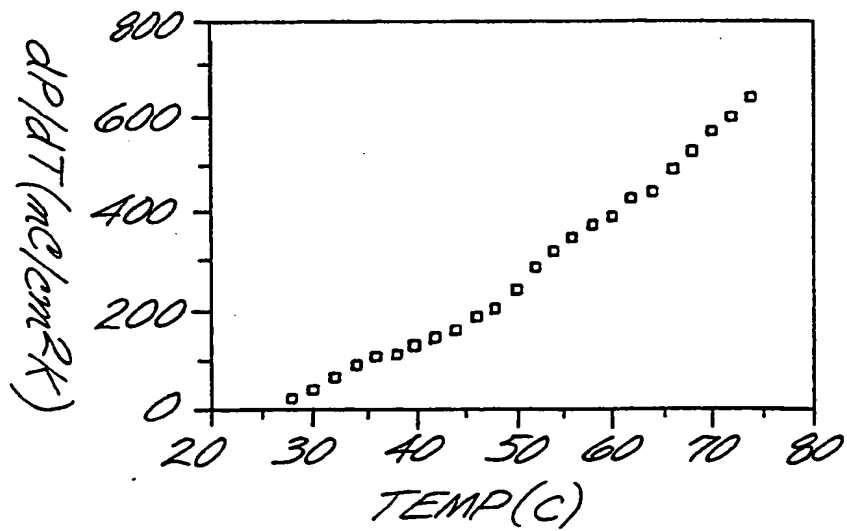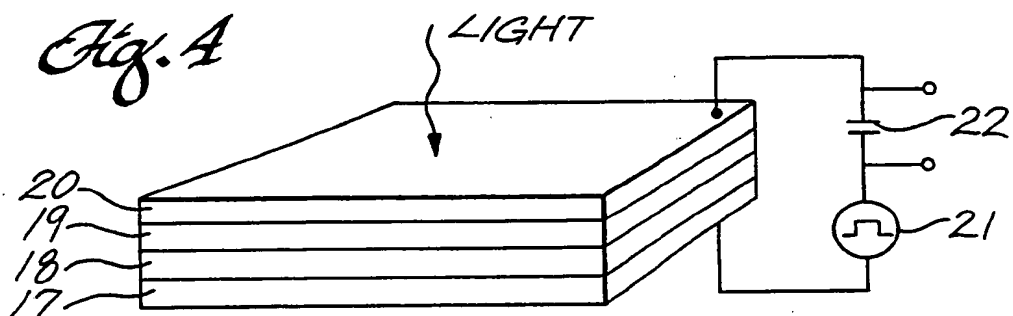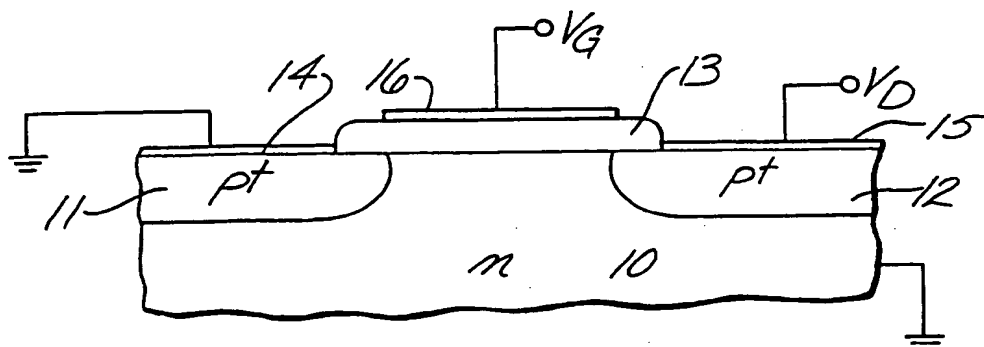a thin film of amorphous ferroelectric material deposited on the substrate.
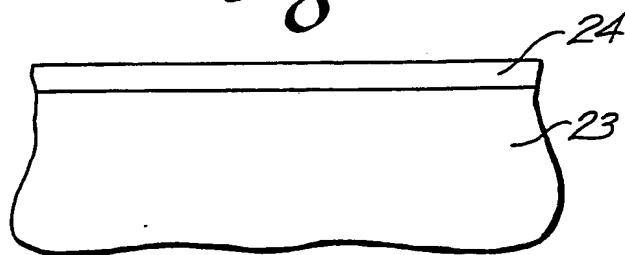
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Fig.1

Fig.2

Fig. 3

Fig. 4

LIGHT

Fig. 5

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C04B 35/46; B05D 5/12; B05D 3/12; B05D 3/02; C04B 35/49
US CL :501/134,135,136,137,138; 427/100,126.3,346,376.2,385.5
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Searched APS for inventors also terms "amorphous" or "glassy" or "non-crystalline" and "terraelectric" or "piezoelectric"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J. Appl. Phys., 1 September 1988, Yi et al., Preparation of $Pb(Zr,Ti)O_3$ thin films by Sol gel processing: Electrical, optical, and electro-optic properties, p. 2717-2724. See entire document.	1-5,11-14
A	Mat. Res. Inc. Symp. Proc., 1986, Budd et al., The Effect of Hydrolysis Conditions on the Characteristics of $PbTiO_3$ Gels and Thin Films, p. 317-322.	
A	Journal of Non-Crystalline Solids, 1988, Hirane, Formation of $LiNbO_3$ Films by Hydrolysis of Metal Alkoxides, p. 538-541.	
A	Journal of Materials Science, 1984, Fukushima Preparation of Ferroelectric P2T Films by Thermal Decomposition of Organ-Metallic Compounds, p. 595-598.	
A	US, A, 3,660,155 (Mackenzie) 02 May 1972.	

☐ Further documents are listed in the continuation of Box C.   ☐ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be part of particular relevance

"E" earlier document published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
10 AUGUST 1992	2 4 SEP 1992

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